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- (51) INTL.CL. ⁵ C07C-213/10; C07C-215/10
- (19) (CA) APPLICATION FOR CANADIAN PATENT (12)
- (54) Method for Inhibiting Color Contamination in
Ethanolamine Compounds
- (72) Martin, John F. - U.S.A. ;
- (73) Betz Laboratories, Inc. - U.S.A. ;
- (30) (US) 07/703,946 1991/05/22
- (57) 16 Claims

Notice: The specification contained herein as filed

Canada

CCA 3254 (10-89) 41

-17-

ABSTRACT

The present invention is directed towards methods for inhibiting color formation in ethanolamine compounds. Color formation and contamination can be inhibited by adding an effective amount of an amine compound.

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METHOD FOR INHIBITING COLOR CONTAMINATION
IN ETHANOLAMINE COMPOUNDS

FIELD OF THE INVENTION

5 The present invention is directed to a method of inhibiting color formation and contamination in ethanolamine compounds. More specifically, the present invention is directed to a method of using amine compounds to inhibit the formation of oxygen containing compound impurities which cause color contamination in ethanolamine compounds.

10 BACKGROUND OF THE INVENTION

Ethanolamine compounds, which include monoethanolamine, diethanolamine and triethanolamine, are produced commercially by reacting ethylene oxide, ammonia and water in a tubular reactor.

15 Oftentimes, the compounds generated by this method exhibit an undesirable color and color instability developed over a period of time. Nickel contained in the process system metallurgy is thought to catalyze dehydrogenation reactions of by-product ethylene glycol. It is thought that these reactions form oxygen containing carbonyl compounds such as aldehydes and ketones.

20 The aldehyde compounds can undergo the aldol-condensation reactions in the process system environment. Nickel may also catalyze the direct decomposition of the ethanolamine compounds, further forming carbonyl compounds.

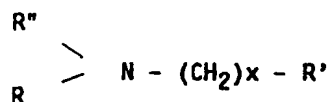
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One theory postulates that these condensation polymerization contaminants thus formed can cause color contamination problems in the finished ethanolamine product.

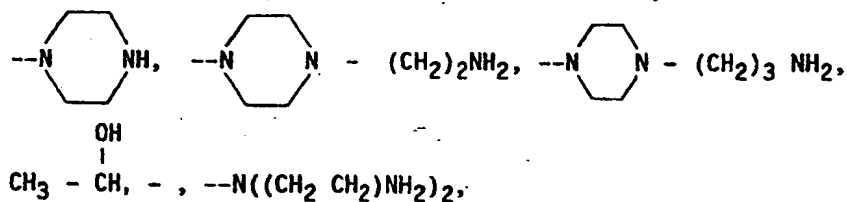
- 5 Avoidance of color contamination increases the value of the ethanolamine compound to the producer and minimizes the off-specification product manufactured.

SUMMARY OF THE INVENTION

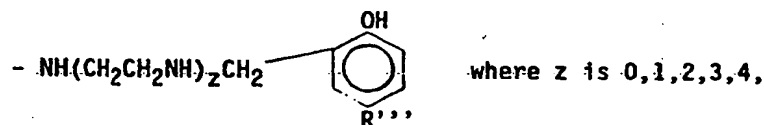
- 10 The present invention provides for a method for inhibiting color formation in ethanolamine compounds comprising adding to said ethanolamine compounds an effective amount for the purpose of an amine compound of the formula



- 15 wherein R is H or OH; R' is $-\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_y\text{H}$ where y is an integer from about 0 to about 20,

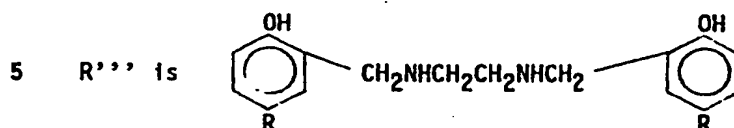
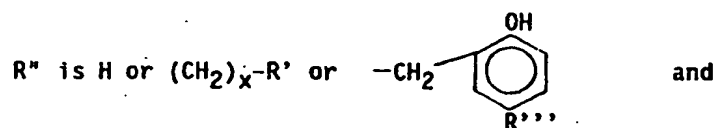


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2061718

-3-



and x is about 1 to about 3.

10 While effective in all ethanolamine compounds, the method of the present invention is particularly effective at inhibiting color formation in monoethanolamine, diethanolamine and triethanolamine.

The present method entails ensuring that the amine compounds are present in the ethanolamine reactor effluent.

DESCRIPTION OF THE RELATED ART

15 United States Patent 4,952,301, Awbrey, August 1990, discloses a method of inhibiting the formation of polymeric fouling deposits formed during the caustic washing of hydrocarbons. This method employs the use of an ethylenediamine compound.

-4-

United States Patent 3,819,710, Jordan, June 1974,
discloses a process for improving the color and color stability of
ethanolamine compounds. This process comprises hydrogenation of
crude mono - , di and triethanolamines using selected catalysts at
5 specific temperatures and pressures.

United States Patent 4,673,762, Paslean et al., June 1987,
discloses a method for decolorizing ethanolamine compounds. This
method employs adding to the ethanolamine compound an alkyleneoxide
such as ethylene oxide.

10 Japanese Patent Publication No. 1977 - [Showa 52]-28,770
discloses a method of decoloring ethyleneamines and alkanolamines.
This method is accomplished by heat treatment of the amine compound
in the presence of hydrogen and a catalyst. The catalyst can be
selected from a nickel-type, cobalt-type or nickel-cobalt-mixed
15 type hydrogenation catalyst.

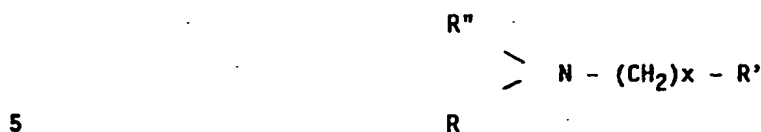
European patent registration A1 0,004,015 discloses a
process for the manufacture of colorless ethanolamines. This
process entails carrying out the ethylene oxide, ammonium, water
reaction in the presence of phosphorous acid or hypophosphorous
20 acid or their compounds.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides for a method for inhibiting
color formation in ethanolamine compounds comprising adding to said

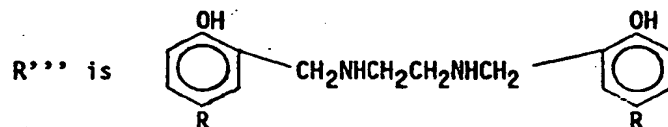
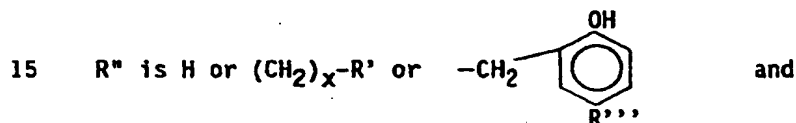
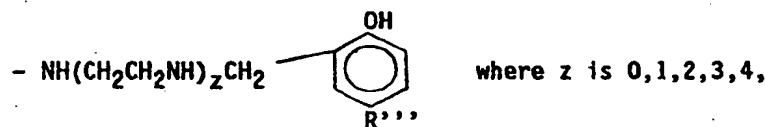
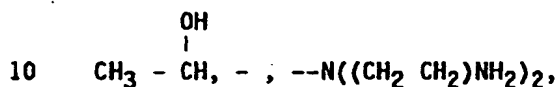
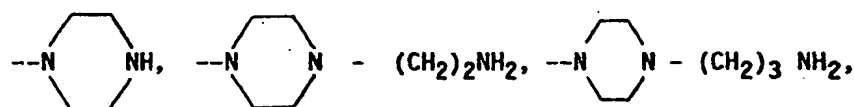
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ethanolamine compounds an effective amount for the purpose of an amine compound of the formula



wherein R is H or OH; R' is $-\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_y\text{H}$

where y is an integer from about 0 to about 20,



and x is about 1 to about 3.

-6-

Of these compounds, tetraethylenepentamine is preferred. In addition, exemplary compounds include diethylenetriamine and triethylenetetramine. The tetraethylenepentamine is preferred as it possesses a higher boiling point than the other two compounds and thus can inhibit color formation at higher temperatures.

These amine compounds are also ashless compounds. This makes their use desirable as industry is moving away from ash containing compounds due to the clean-up costs involved.

These color inhibiting compounds can be added to the ethanolamine compounds as neat materials or in solution form. The preferred method of addition is as an aqueous solution.

The treatment should be added to the ethanolamine in sufficient quantity to ensure there is enough of the amine compound present to react with all the undesirable carbonyl contaminants. Treatment dosages in the range of from about 1 part per million to about 10,000 parts per million parts of ethanolamine compound may be employed. Preferably, the amine compound is added in a range of about 5 parts per million to about 5000 parts per million parts of the ethanolamine compound to be treated.

The invention will be further illustrated by the following examples which are intended merely for purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it may be practiced.

2061718

-7-

EXAMPLESExample 1

In a 17 ml test tube, 10.0 ml of triethanolamine was added. 40 ul of treatment (160 ul of 25% solution) was also added along with a piece of steel. The remaining 7 ml of air space was then purged with argon for 60 seconds and then the cap was securely fastened. The test tube was then placed in a silicone oil bath at the appropriate temperature for the specified time indicated in the table. The time in days represents how many days since the reaction was started. The yellow to brown colors were then compared visually. The results of this first test appear in Table I.

TABLE I

Triethanolamine color development		
310 stainless steel		
4,000 parts per million actives		
Days Since Reaction Started	Temperature of Bath (°C)	Order of Color (Darkest to Lightest)
5	144	HS > TETA > NP > Blank, Blank No SS
7	204	HS > Blank No SS > TETA, NP, Blank
8	204	Blank No SS > HS > Blank > NP > TETA
9	204	Blank No SS > HS > Blank > NP > TETA

25 HS = Hydroxylamine sulfate
 NP = Nonylphenol
 TETA = Triethylenetetramine
 Blank No SS = Blank run with no stainless steel present.

-8-

The results of this test indicate that triethylene-tetramine is more effective at inhibiting color formation than the blank runs over a greater length of time and temperature.

Example 2

- 5 The procedure of example 1 was followed here. These results are shown in Table II.

TABLE II

Triethanolamine color development
4000 parts per million active at 168°C

10	Days Since Reaction Started	Order of Color (Darkest to Lightest)
----	--------------------------------------	---

With 310 SS Present

15	2	HS > TETA > EDA > Blank > NP > DETA = TEPA
	4	HS > TETA > EDA > Blank > NP > DETA = TEPA

Without 310 SS Present

	2	HS > EDA > NP > Blank = TETA = DETA = TEPA
	4	HS > Blank > NP > EDA = TETA = DETA = TEPA

20	HS =	Hydroxylamine Sulfate
	EDA =	Ethylenediamine
	NP =	Nonylphenol
	TETA =	Triethylenetetramine
	DETA =	Diethylenetriamine
25	TEPA =	Tetraethylenepentamine

2061718

-9-

The polyamines diethylenetriamine and tetraethylenepentamine were always less colored than the blanks. The polyamines ethylenediamine and triethylenetetramine proved better than the blanks at longer heating periods with no steel present.

5 Example 3

The procedure of example 1 was followed. The tubes were then wiped clean and inserted into a Hach spectrophotometer set at 410nm and calibrated with an unheated, untreated triethanolamine sample. The results are presented in Table III as % transmittance (%T).

TABLE III

Triethanolamine Color Development
4000 parts per million active at 190°C
No 310 SS present

15	Treatment	%T 24 Hours	%T 48 Hours	%T 62 Hours	%T 24 Hours
		-----Argon Purged-----			Air Purged
20	None	3.5,3.0	1.0,2.5	0.7	0.2
	EDA	-	64.0	-	4.0
	DETA	73.0	63.0	-	7.5

2061718

-10-

TABLE III (Cont'd)

Treatment	%T 24 Hours	%T 48 Hours	%T 62 Hours	%T 24 Hours
	-----Argon Purged-----			Air Purged
5 TEPA		58.5	-	11.0
AEP	44.0	-	-	-
BISAPP	66.5	-	-	-
TREN	27.0	-	-	-
HPHA	25.0	-	-	-
10 MD	35.0	-	-	-

EDA = Ethylenediamine

DETA = Diethylenetriamine

TETA = Triethylenetetramine

TEPA = Tetraethylenepentamine

15 AEP = N-(2-aminoethyl)piperazine

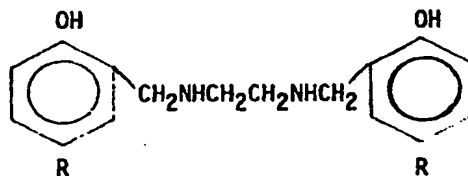
BISAPP = N,N'-bis(3-aminopropyl)piperazine

TREN = Tris(2-aminoethyl)amine

HPHA = Hydroxypropylhydroxylamine

MD =

20



wherein R is H or OH

25 These results show that the polyamines provide high percent transmittance which is indicative of inhibition of color formation.

Example 4

The procedure of example 3 was followed except small pieces of carbon steel were present. These results are shown in Table IV.

2061718

-11-

TABLE IV

Triethanolamine color development
4000 parts per million active at 190°C
Argon Purged

5	Treatment	1010 Carbon Steel		9 CR1MO Carbon Steel
		%T 24 Hours	%T 48 Hours	%T 62 Hours
	None	3.0	3.5	0.0
	DETA	23.5	40.0	1.0
10	TETA	24.0	36.0	1.0
	TEPA	38.0	52.0	1.0

DETA = Diethylenetriamine
TETA = Triethylenetetramine
TEPA = Tetraethylenepentamine

- 15 These results again show that the polyamines inhibited color formation in the ethanolamines.

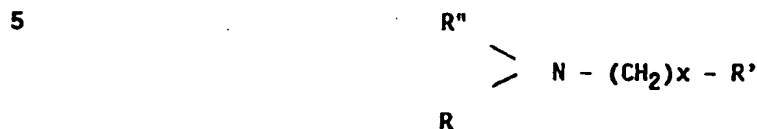
While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art.

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-12-

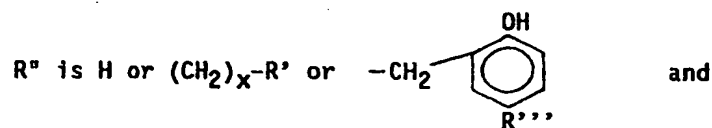
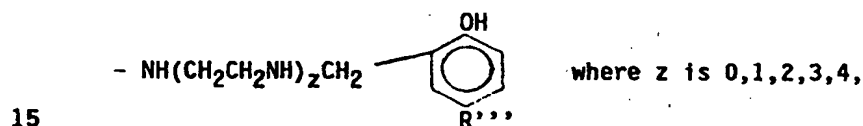
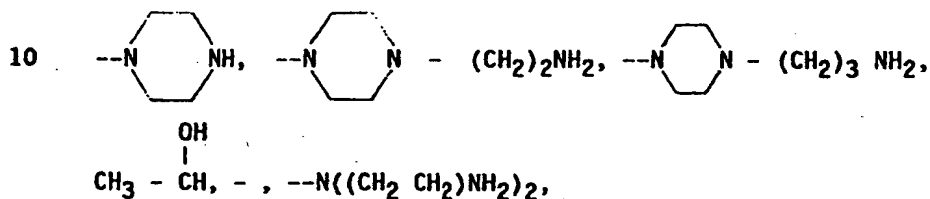
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for inhibiting color formation in ethanolamine compounds comprising adding to said ethanolamine compound an effective amount for the purpose of an amine compound of the formula



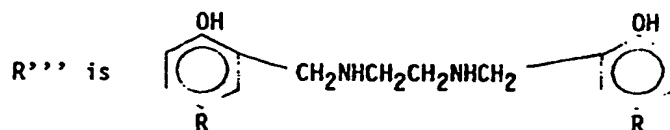
wherein R is H or OH; R' is $-\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_y\text{H}$

where y is an integer from about 0 to about 20,



2061718

-13-



and x is about 1 to about 3.

2. The method as claimed in claim 1 wherein said amine compound is diethylenetriamine.

3. The method as claimed in claim 1 wherein said amine compound is triethylenetetramine.

4. The method as claimed in claim 1 wherein said amine compound is tetraethylenepentamine.

5. The method as claimed in claim 1 wherein said amine compound is added to said ethanolamine compound from about 1 part per million to about 10,000 parts per million parts of said ethanolamine compound.

6. The method as claimed in claim 1 wherein said amine compound is added to said ethanolamine compound from about 5 parts per million to about 5000 parts per million parts of said ethanolamine compound.

7. The method as claimed in claim 1 wherein said ethanolamine compound is monoethanolamine.

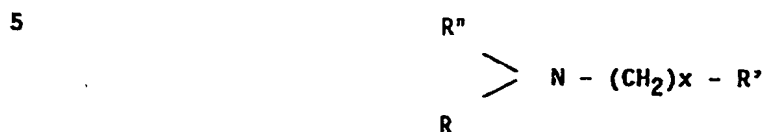
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-14-

8. The method as claimed in claim 1 wherein said ethanolamine compound is diethanolamine.

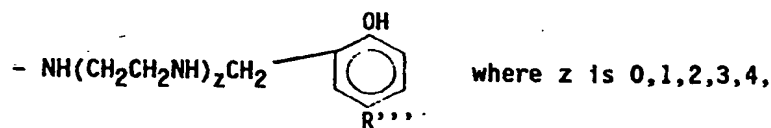
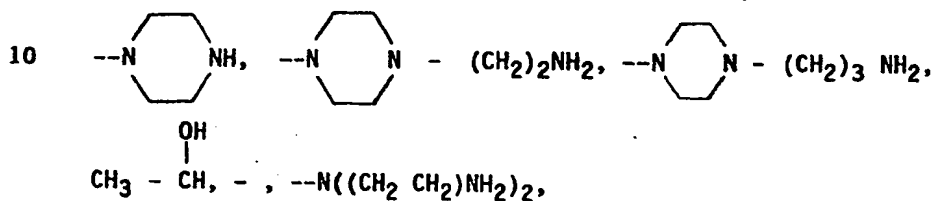
9. The method as claimed in claim 1 wherein said ethanolamine compound is triethanolamine.

10. A method for inhibiting color formation in ethanolamine compounds comprising adding to said ethanolamine compound an effective amount for the purpose of at least two amine compounds of the formula



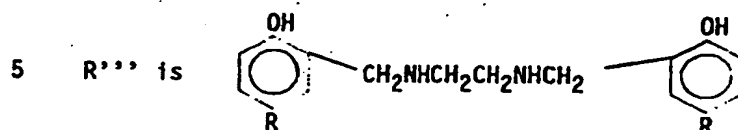
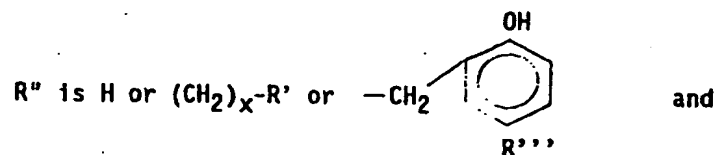
wherein R is H or OH; R' is $-\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_y\text{H}$

where y is an integer from about 0 to about 20,



2061718

-15-



and x is about 1 to about 3.

11. The method as claimed in claim 10 wherein said mixture consists essentially of diethylenetriamine, triethylenetetramine and tetraethylenepentamine.

12. The method as claimed in claim 10 wherein said mixture is added to said ethanolamine compound from about 1 part per million to about 10,000 parts per million parts of said ethanolamine.

13. The method as claimed in claim 10 wherein said mixture is added to said ethanolamine compound from about 5 parts per million to about 5000 parts per million parts of said ethanolamine compound.

14. The method as claimed in claim 10 wherein said ethanolamine compound is monoethanolamine.

-16-

15. The method as claimed in claim 10 wherein said ethanolamine compound is diethanolamine.

16. The method as claimed in claim 10 wherein said ethanolamine compound is triethanolamine.